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# FUEL REFORMER FOR FUEL CELL

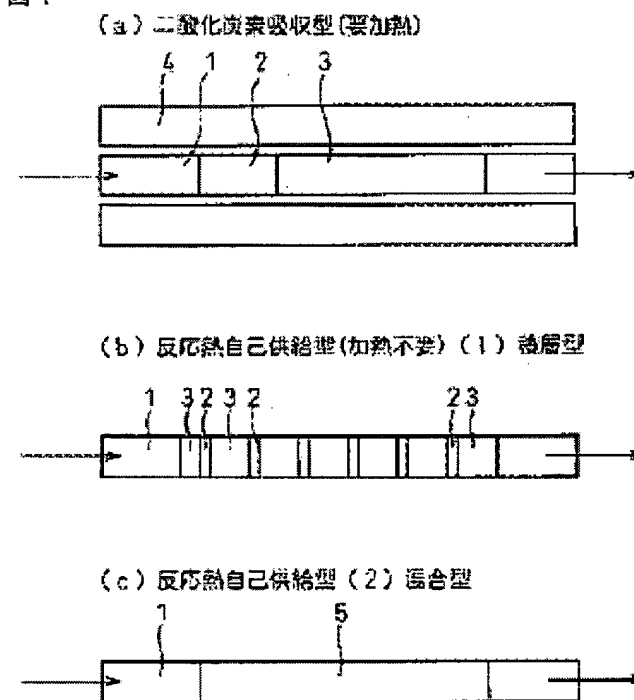
**Patent number:** JP2002208425  
**Publication date:** 2002-07-26  
**Inventor:** KATO YUKITAKA; YOSHIZAWA YOSHIO  
**Applicant:** RIKOGAKU SHINKOKAI  
**Classification:**  
- international: H01M8/06; C01B3/32; C01B3/38; C01B3/56  
- european:  
**Application number:** JP20010003054 20010110  
**Priority number(s):**

## Abstract of JP2002208425

**PROBLEM TO BE SOLVED:** To provide a fuel reformer which can generate high-purity hydrogen or even, does not need outer heating.

**SOLUTION:** The fuel reformer generates hydrogen from fuel and steam, and is equipped with a fuel reforming catalyst layer filled with steam reforming catalyst of fuel, a reforming fuel gas supply means introducing fuel and reforming fuel gas containing steam to the fuel reforming catalyst layer, a reforming fuel gas exhausting means exhausting hydrogen principal component gas generated by steam reforming from the fuel reforming catalyst layer, and a metal oxide layer provided at downstream of the fuel reforming catalyst layer to absorb carbon dioxide contained in the reforming fuel.

図 1



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## CLAIMS

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### [Claim(s)]

[Claim 1] The fuel reforming catalyst layer which is the fuel refining machine which manufactures hydrogen from a fuel and a steam, and was filled up with the catalyst for steam reforming of a fuel, A fuel gas supply means for refining to introduce the fuel gas for refining containing a fuel and a steam into this fuel reforming catalyst layer, The fuel refining machine for fuel cells which comes to have the metal oxide layer prepared in the lower stream of a river of this fuel reforming catalyst layer in order to absorb the carbon dioxide contained in a refining fuel gas blowdown means to discharge the hydrogen principal component gas generated by steam reforming from this fuel reforming catalyst layer, and this refining fuel.

[Claim 2] The fuel reforming catalyst layer which is the fuel refining machine which manufactures hydrogen from a fuel and a steam, and was filled up with the catalyst for steam reforming of a fuel, A fuel gas supply means for refining to introduce the fuel gas for refining containing a fuel and a steam into this fuel reforming catalyst layer, In order to absorb the carbon dioxide contained in a refining fuel gas blowdown means to discharge the hydrogen principal component gas generated by steam reforming from this fuel reforming catalyst layer, and this refining fuel The fuel refining machine for fuel cells to which is equipped with the metal oxide layer prepared in the lower stream of a river of this fuel reforming catalyst layer, and it comes to carry out the at least 2 or more set laminating of this fuel reforming catalyst layer and this metal oxide layer by turns.

[Claim 3] The fuel refining machine for fuel cells which comes to have a fuel-gas supply means for refining introduce into this fuel reforming catalyst layer the fuel gas for refining containing the fuel reforming catalyst layer, the fuel, and the steam which are the fuel refining machine which manufactures hydrogen from a fuel and a steam, and were filled up with the catalyst for steam reforming and the metallic oxide of a fuel, and a refining fuel-gas blowdown means discharge the hydrogen principal component gas generated by steam reforming from this fuel reforming catalyst layer.

[Claim 4] The refining approach of the fuel characterized by introducing a fuel and a steam into this fuel reforming catalyst layer by preparing a metal oxide layer in the lower stream of a river of a fuel reforming catalyst layer, introducing into this metal oxide layer the hydrogen and the carbon dioxide which were subsequently generated, making a carbon dioxide absorb selectively in the refining approach of a fuel and the fuel which manufactures hydrogen from a steam, and making hydrogen flow out of this metal oxide layer.

[Claim 5] In the refining approach of a fuel and the fuel which manufactures hydrogen from a steam,

the at least 2 or more set laminating of a fuel reforming catalyst layer and the metal oxide layer of the lower stream of a river is carried out by turns. While introducing a fuel and a steam into this fuel reforming catalyst layer, introducing into this metal oxide layer the hydrogen and the carbon dioxide which were subsequently generated, making a carbon dioxide absorb selectively and making hydrogen flow out of this metal oxide layer. The refining approach of the fuel characterized by supplying further the heat of reaction generated in the case of this absorption as refining heat of reaction to this down-stream reforming catalyst layer.

[Claim 6] The refining approach of the fuel characterized by preparing the fuel reforming catalyst layer which mixed the metallic oxide for the catalyst in the refining approach of a fuel and the fuel which manufactures hydrogen from a steam, introducing a fuel and water into this reforming catalyst layer, and making only hydrogen flow out of this fuel reforming catalyst layer substantially.

[Claim 7] The refining approach of the fuel characterized by advancing decarboxylation of the metal carbonate which heated and generated this fuel reforming catalyst layer from the exterior after reaction termination in claim 6, collecting carbon dioxides, and reproducing a metallic oxide.

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the fuel refining approach using the fuel refining machine for fuel cells and it using a metallic oxide in more detail about the fuel refining machine for fuel cells.

[0002]

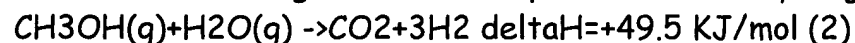
[Description of the Prior Art] The fuel reformer which generates hydrogen and a carbon dioxide from a fuel and water (steam), such as methane and a methanol, is known as equipment for supplying fuel gas to a fuel cell. The fuel gas containing hydrogen is supplied to a fuel cell at a cathode side, the oxidation gas containing oxygen is supplied at an anode plate side, and electromotive force is acquired according to the electrochemical reaction produced on two poles.

[0003] First, in the fuel reformer using methane content gas and a steam, generally the following methane refining reactions are performed and hydrogen and a carbon dioxide are manufactured.



This reaction is endothermic reaction, and a reaction is performed at about 800 degrees C using the packed bed reactor into which the nickel catalyst usually went, carrying out fuel gas heating from the outside. Four mols are carried out for hydrogen at a rate of one mol, refining of the fuel is carried out for a carbon dioxide by the reaction, and this mixed gas is used as a fuel with a fuel cell by it.

[0004] On the other hand, in the fuel reformer using a methanol and a steam, generally the following methanol-reforming reactions are performed and hydrogen and a carbon dioxide are manufactured.



This reaction is endothermic reaction, and a reaction is performed using the packed bed reactor into which the nickel catalyst usually went like the case of methane, carrying out fuel gas heating from the outside. In this case, it is [0005] for which a reaction is performed at about 200-300 degrees C, three mols are carried out for hydrogen at a rate of one mol, refining of the fuel is carried out for a carbon dioxide, and this mixed gas is used as a fuel with a fuel cell.

[Problem(s) to be Solved by the Invention] Thus, since it is necessary to make heat energy supply for example, and the method of forming a burner and a heater and performing heat tracing is usually performed, the above-mentioned refining reaction is endothermic reaction and it is further generated collectively by the carbon dioxide in order to advance a refining reaction, in order to raise the engine performance of a fuel cell, high concentration hydrogen is desired.

[0006] Then, this invention person examined many things so that he may get the fuel refining machine

which can generate the hydrogen of a high grade or does not need heat tracing on it, and he reached this invention.

[0007]

[Means for Solving the Problem] The fuel refining machine for fuel cells of the 1st mode in this invention The fuel reforming catalyst layer which is the fuel refining machine which manufactures hydrogen from a fuel and a steam, and was filled up with the catalyst for steam reforming of a fuel, A fuel gas supply means for refining to introduce the fuel gas for refining containing a fuel and a steam into this fuel reforming catalyst layer, In order to absorb the carbon dioxide contained in a refining fuel gas blowdown means to discharge the hydrogen principal component gas generated by steam reforming from this fuel reforming catalyst layer, and this refining fuel, let the fuel refining machine for fuel cells which comes to have the metal oxide layer prepared in the lower stream of a river of this fuel reforming catalyst layer be a summary.

[0008] In this invention, although the fuel by which refining is carried out has common hydrocarbons and methanols, such as methane content gas, such as methane and natural gas, a gasoline, naphtha, gas oil, and LP gas, it explains the case of methane and a methanol in the following explanation. Moreover, what reacts with a carbon dioxide and generates a metal carbonate as the above-mentioned metallic oxide is used, and oxides, such as calcium, magnesium, copper, iron, and nickel, are suitable. In order to obtain the fuel refining machine which does not need heat tracing, especially in the case of methane, in the case of a calcium oxide and a methanol, a magnesium oxide is suitable, although the selection is based on the class of fuel etc.

[0009] In the fuel refining machine constituted as mentioned above, if methane and a steam are introduced into this methane reforming catalyst layer, hydrogen and a carbon dioxide will be generated at about 800 degrees C. Subsequently, if these are introduced into a calcium-oxide layer, a calcium oxide will react with a carbon dioxide near 800 degree C, and a calcium carbonate will be generated.



Thus, a carbon dioxide is selectively absorbed by the calcium-oxide layer, and hydrogen flows out of this calcium layer. Therefore, since high-concentration hydrogen is obtained, the engine performance of a fuel cell improves. Furthermore, it can collect, without emitting a carbon dioxide to atmospheric air. On the other hand, if a methanol and a steam are introduced into this methanol reforming catalyst layer, in order to consider as the reaction rate of practical use level, hydrogen and a carbon dioxide will be generated at about 200 degrees C - suitable 300 degrees C (at least 100 degrees C or less of the methanol-reforming reactions itself advance in reaction balance). Subsequently, if these are introduced into a magnesium-oxide layer, a magnesium oxide will react with a carbon dioxide near 300 degrees C - 450 degree C, and a magnesium carbonate will be generated.

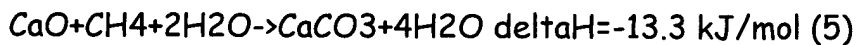
[0010]



Thus, a carbon dioxide is selectively absorbed by the magnesium-oxide layer, and hydrogen flows out of this magnesium layer. Therefore, since high-concentration hydrogen is obtained, the engine performance of a fuel cell improves. Furthermore, it can collect, without emitting a carbon dioxide to atmospheric air. The fuel refining machine for fuel cells of the 2nd mode in this invention The fuel reforming catalyst layer which is the fuel refining machine which manufactures hydrogen from a fuel and a steam, and was filled up with the catalyst for steam reforming of a fuel, A fuel gas supply means

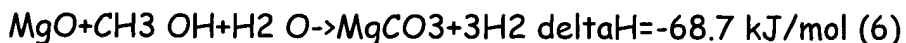
for refining to introduce the fuel gas for refining containing a fuel and a steam into this fuel reforming catalyst layer, In order to absorb the carbon dioxide contained in a refining fuel gas blowdown means to discharge the hydrogen principal component gas generated by steam reforming from this fuel reforming catalyst layer, and this refining fuel It has the metal oxide layer prepared in the lower stream of a river of this fuel reforming catalyst layer, and let the fuel refining machine for fuel cells to which it comes to carry out the at least 2 or more set laminating of this fuel reforming catalyst layer and this metal oxide layer by turns be a summary. In the fuel refining machine constituted as mentioned above, if methane and a steam are introduced into this methane reforming catalyst layer, hydrogen and a carbon dioxide will be generated at about 800 degrees C. Since the laminating of this catalyst bed is carried out to the calcium-oxide layer of the lower stream of a river by turns, the generated carbon dioxide is absorbed in a down-stream calcium-oxide layer. At this time, the exothermic reaction heat (178.1 kJ/mol) of carbonation generates as mentioned above. Since this heat of formation is larger than the necessary heating value (-164.8 kJ/mol) of methane refining endothermic reaction, consecutive refining heat of reaction can be supplied with carbonation heat. The following reaction formulae are materialized [ in / whole / a layer ].

[0011]



That is, there is generation of heat of 13.3 kJ/mol and this reaction advances without the heat supply from the outside. Thus, it can realize that this fuel refining machine can carry out self-supply of the required heat without heating from the outside. On the other hand, if a methanol and a steam are introduced into this methanol reforming catalyst layer, hydrogen and a carbon dioxide will be suitably generated at about 200 degrees C - 300 degrees C. Since the laminating of this catalyst bed is carried out to the magnesium-oxide layer of the lower stream of a river by turns, the generated carbon dioxide is absorbed in a down-stream magnesium-oxide layer. At this time, the exothermic reaction heat (118.2 kJ/mol) of carbonation generates as mentioned above. Since this heat of formation is larger than the necessary heating value (-49.5 kJ/mol) of methanol-reforming endothermic reaction, consecutive refining heat of reaction can be supplied with carbonation heat. The following reaction formulae are materialized [ in / whole / a layer ].

[0012]



That is, there is generation of heat of 68.7 kJ/mol and this reaction advances without the heat supply from the outside. Thus, it can realize that this fuel refining machine can carry out self-supply of the required heat without heating from the outside.

[0013] Furthermore, the fuel refining machine for fuel cells of the 3rd mode in this invention The fuel reforming catalyst layer which is the fuel refining machine which manufactures hydrogen from a fuel and a steam, and was filled up with the catalyst for steam reforming and metallic oxide of a fuel, Let the fuel refining machine for fuel cells which comes to have a fuel gas supply means for refining to introduce the fuel gas for refining containing a fuel and a steam into this fuel reforming catalyst layer, and a refining fuel gas blowdown means to discharge the hydrogen principal component gas generated by steam reforming from this fuel reforming catalyst layer be a summary. In this mode, since the methane reforming catalyst layer is mixed and filled up with the catalyst and the calcium oxide, fuel refining of a more prompt heat-of-reaction self-supply mold becomes possible. In this mode, since the methanol reforming catalyst layer is mixed and filled up with the catalyst and the

magnesium oxide, fuel refining of a more prompt heat-of-reaction self-supply mold becomes possible. [0014]

[Embodiment of the Invention] Hereafter, the case where methane content gas is first used as fuel gas in this invention is explained with a drawing. Drawing 1 is the mimetic diagram showing the refining machine of three modes of the above 1-3rds in this invention. a is the refining machine of the carbon-dioxide absorption mold which requires heating, and methane is introduced into a coil (1) with a steam as methane content gas. The coil (1) is held with the heating furnace (4) at predetermined temperature, and the catalyst bed (2) is filled up with nickel support alumina as a catalyst for steam reforming. In this catalyst bed, a refining reaction is carried out at about 800 degrees C, the generation gas containing hydrogen and a carbon dioxide flows out, and it is introduced into the metal oxide layer (3) filled up with the down-stream calcium oxide. A carbon dioxide is absorbed selectively and high-concentration hydrogen flows out of a metal oxide layer there. The above-mentioned catalyst is not limited to the above-mentioned nickel, further, support is also replaced with an alumina and a silica etc. can be used for it for it. b shows the laminating mold refining machine which carried out the 2 or more set laminating of the metal oxide layer (3) by which calcium-oxide restoration was carried out with nickel support catalyst bed (2) by turns, and c shows the hybrid model refining machine which has the catalyst / metallic-oxide mixing layer (5) which mixed the calcium oxide with nickel support alumina. Each of b and c is heat-of-reaction self-supply molds, does not need heating fundamentally but is equipped with the preheater (not shown) of the sake at the time of a start.

[0015] Also in fuel refining of this invention, the carbon monoxide of a minute amount is generated like the conventional fuel refining. Since this carbon monoxide carries out poisoning of the catalyst and has an adverse effect, it needs to convert this into a carbon dioxide. Therefore, it is converted into a carbon dioxide by the convertor prepared in the refining machine lower stream of a river. In the refining machine of this invention, in order that the carbon dioxide generated by nickel catalyst bed may be absorbed by carbonation and the concentration may decrease, the reaction of carbon-dioxide-izing of a carbon monoxide advances better in balanced theory. For this reason, generating of a carbon monoxide is controlled. Since a carbon monoxide carries out poisoning of the electrode catalyst (platinum system) of a fuel cell and a cell property is reduced, although the carbon monoxide shift coverter is formed in the lower stream of a river of a refining machine, according to this invention, reduction or it can usually be made unnecessary for the load to this transformer.

[0016] Drawing 2 shows the progressive of the main reactions in the fuel refining machine of this invention by the chemical reaction equilibrium line, and shows the balanced relation between a calcium oxide/carbon dioxide, a calcium oxide/water, and a fuel refining reaction. A calcium oxide / carbon-dioxide system is the reactions of this \*\*, and a calcium oxide/drainage system is competitive reactions expected from the gas to be used. The pressure P of an axis of ordinate shows the carbon-dioxide pressure in each reaction, and the water-vapor-pressure force, and shows the degree of completion of whenever [ decomposition ] (leftward reaction) (it decomposes so well that P is large). Only a refining reaction shows the reaction equilibrium constant K. For example, near 700 degree C, a calcium carbonate is hardly disassembled. That is, carbonation of a calcium oxide progresses well. Moreover, it turns out that a fuel refining reaction advances rightward (hydrogen generation side). On the other hand, since it decomposes and most calcium hydroxides turn into a calcium oxide, the water absorption to a calcium oxide hardly happens. Performing a calcium oxide and a carbonation reaction can check thermodynamically the carbon dioxide which the refining reaction progressed well and was



generated from this in this temperature region.

[0017] Furthermore, drawing 3 shows the reaction layer temperature change accompanying fluctuation of a carbonation pressure in the initial temperature of 650 degrees C of a reaction. That is, in the packed-bed mold reactor of about 1kg of calcium-oxide reaction samples, if a carbon dioxide is introduced into a 650-degree C reaction layer in reaction-time 0 minute the first stage, a reaction will advance promptly. And the temperature rise of the reaction layer is rapidly carried out to 900-1000 degrees C with heat of reaction. The absorption (carbonation) to the calcium oxide of the carbon dioxide near about 700-800 degree C from this fully advances, and it is shown that self-heat-of-reaction supply is possible.

[0018] On the other hand, although it changes to methane/calcium oxide as above-mentioned, it changes to a methanol/magnesium oxide and reaction temperature differs in using a methanol fuel in this invention, above-mentioned drawing 1 a, b, and c corresponds as it is. Drawing 4 , When using a methanol fuel, a chemical reaction equilibrium line shows the progressive of the main reactions in the fuel refining machine of this invention, and the balanced relation between a magnesium oxide/carbon dioxide, a magnesium oxide/water, and a fuel refining reaction is shown. A magnesium oxide / carbon-dioxide system is the reactions of this \*\*, and a magnesium oxide/drainage system is competitive reactions expected from the gas to be used. The pressure P of an axis of ordinate shows the carbon-dioxide pressure in each reaction, and the water-vapor-pressure force, and shows the degree of completion of whenever [ decomposition ] (leftward reaction) (it decomposes so well that P is large). Only a refining reaction shows the reaction equilibrium constant K. For example, near 300 degree C, a magnesium carbonate is hardly disassembled. That is, carbonation of a magnesium oxide progresses well. Moreover, it turns out that a fuel refining reaction advances rightward (hydrogen generation side). On the other hand, since it decomposes and most magnesium hydroxides turn into a magnesium oxide, the water absorption to a magnesium oxide hardly happens. Performing a magnesium oxide and a carbonation reaction can check thermodynamically the carbon dioxide which the refining reaction progressed well and was generated from this in this temperature region.

[0019] Since heating decomposes by ordinary pressure and the magnesium carbonate generated by the formula (6) returns to a magnesium oxide, it can be used for fuel refining for the second time. In addition, the heat of reaction expressed with a formula (2) changes with phases of a reaction raw material. for example, case where a methanol is the liquid phase  $\text{CH}_3\text{OH}(\text{L}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2 + 3\text{H}_2$  the case where both  $\Delta H = +87.0 \text{ KJ/mol}$  (2-2), a methanol, and water are the liquid phase --  $\text{CH}_3\text{OH}(\text{L}) + \text{H}_2\text{O}(\text{L}) \rightarrow \text{CO}_2 + 3\text{H}_2$  It is  $\Delta H = +131.0 \text{ KJ/mol}$  (2-3). The calorific value in the MgO carbonation expressed with a formula (6) is larger than a heating value required for the reaction of a formula (2), and exoergic temperature is also about 300 degrees C. Therefore, the own strength reaction which can fully supply and does not need heat tracing is also possible for the refining heat of reaction of a formula (2). Furthermore, since the calorific value of a formula (6) is larger than a heating value required for the reaction of a formula (2-2), the surplus heat is applicable to evaporation of a methanol. On the other hand, although the heating value of a formula (6) is inadequate for the reaction of the formula (2-3) also containing the heat of vaporization of water, own strength progress of a formula (2-3) also becomes possible by using together the waste heat from a fuel cell (for example, fuel cell for automobiles).

[0020] The fuel refining machine which can generate the hydrogen of a high grade according to this invention, or does not need heat tracing on it can be offered as above-mentioned.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the embodiment of the fuel refining machine of this invention typically.

[Drawing 2] It is drawing showing the chemical reaction equilibrium line of the main reactions in the fuel refining machine of this invention.

[Drawing 3] In the fuel refining machine of this invention, it is drawing showing change of the reaction layer temperature accompanying fluctuation of a carbonation pressure.

[Drawing 4] It is drawing showing the chemical reaction equilibrium line of the main reactions in the fuel refining machine of this invention.

[Description of Notations]

- 1 -- Coil
- 2 -- Catalyst bed
- 3 -- Metal oxide layer
- 4 -- Heating furnace
- 5 -- A catalyst / metallic-oxide mixing layer

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[Translation done.]

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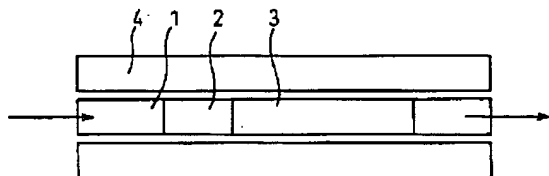
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## DRAWINGS

[Drawing 1]

図 1

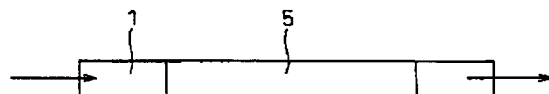
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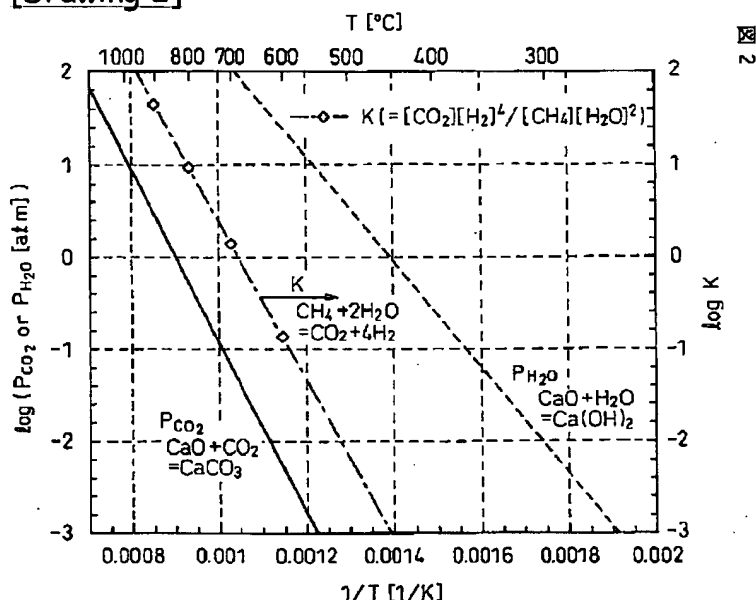
(b) 反応熱自己供給型 (加熱不要) (1) 積層型



(c) 反応熱自己供給型 (2) 混合型

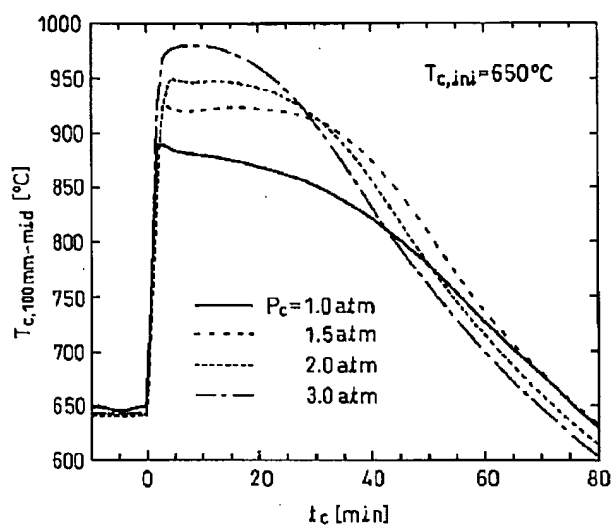


[Drawing 2]



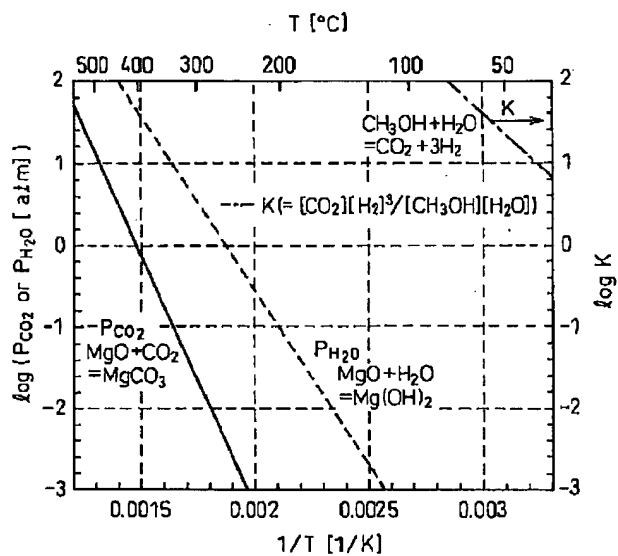
### [Drawing 3]

図 3



### [Drawing 4]

図 4



[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

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特開2002-208425

(P2002-208425A)

(43) 公開日 平成14年7月26日 (2002.7.26)

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C 0 1 B 3/32		C 0 1 B 3/32	A 4 G 1 4 0
	3/38		4 H 0 6 0
	3/56		Z 5 H 0 2 7
# C 1 0 K 1/32		C 1 0 K 1/32	
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(22) 出願日 平成13年1月10日 (2001.1.10)

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最終頁に続く

(54) 【発明の名称】 燃料電池用燃料改質器

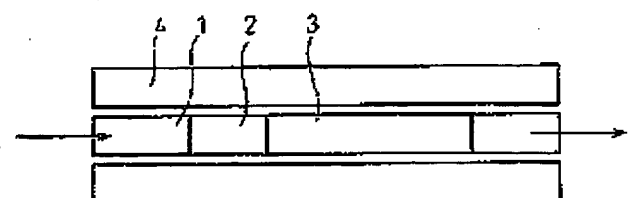
(57) 【要約】

【課題】 高純度の水素が生成でき、もしくはそのうえ外部加熱を必要としない燃料改質器を提供する。

【解決手段】 燃料と水蒸気から水素を製造する燃料改質器であって、燃料の水蒸気改質用触媒を充てんした燃料改質触媒層、燃料および水蒸気を含む改質用燃料ガスを該燃料改質触媒層に導入する改質用燃料ガス供給手段、水蒸気改質により生成する水素主成分ガスを該燃料改質触媒層から排出する改質燃料ガス排出手段、ならびに該改質燃料に含まれる二酸化炭素を吸収するために、該燃料改質触媒層の下流に設けられた金属酸化物層、を備えてなる燃料電池用燃料改質器。

図1

(a) 二酸化炭素吸収型 (要加熱)



(b) 反応熱自己供給型 (加熱不要) (1) 積層型



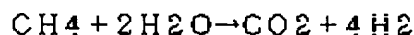
## 【特許請求の範囲】

【請求項1】 燃料と水蒸気から水素を製造する燃料改質器であって、燃料の水蒸気改質用触媒を充てんした燃料改質触媒層、燃料および水蒸気を含む改質用燃料ガスを該燃料改質触媒層に導入する改質用燃料ガス供給手段、水蒸気改質により生成する水素主成分ガスを該燃料改質触媒層から排出する改質燃料ガス排出手段、ならびに該改質燃料に含まれる二酸化炭素を吸収するために、該燃料改質触媒層の下流に設けられた金属酸化物層、を備えてなる燃料電池用燃料改質器。

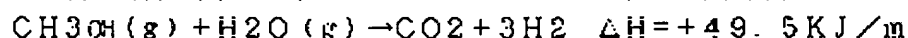
【請求項2】 燃料と水蒸気から水素を製造する燃料改質器であって、燃料の水蒸気改質用触媒を充てんした燃料改質触媒層、燃料および水蒸気を含む改質用燃料ガスを該燃料改質触媒層に導入する改質用燃料ガス供給手段、水蒸気改質により生成する水素主成分ガスを該燃料改質触媒層から排出する改質燃料ガス排出手段、ならびに該改質燃料に含まれる二酸化炭素を吸収するために、該燃料改質触媒層の下流に設けられた金属酸化物層、を備え、該燃料改質触媒層および該金属酸化物層を交互に少なくとも2組以上積層させてなる、燃料電池用燃料改質器。

【請求項3】 燃料と水蒸気から水素を製造する燃料改質器であって、燃料の水蒸気改質用触媒および金属酸化物を充てんした燃料改質触媒層、燃料および水蒸気を含む改質用燃料ガスを該燃料改質触媒層に導入する改質用燃料ガス供給手段、ならびに水蒸気改質により生成する水素主成分ガスを該燃料改質触媒層から排出する改質燃料ガス排出手段、を備えてなる燃料電池用燃料改質器。

【請求項4】 燃料と水蒸気から水素を製造する燃料の改質方法において、燃料改質触媒層の下流に金属酸化物層を設け、燃料と水蒸気を該燃料改質触媒層に導入し、ついで生成した水素および二酸化炭素を該金属酸化物層に導入して二酸化炭素を選択的に吸収させ、該金属酸化物層から水素を流出させることを特徴とする燃料の改質方法。



この反応は吸熱反応であり、通常ニッケル触媒が入った充填層反応器を用い、外部からガス燃料加熱しながら約800℃で反応が行なわれる。反応により、水素が4モル、二酸化炭素が1モルの割合で燃料が改質され、この



o1(2)

この反応は吸熱反応であり、メタンの場合と同様に通常ニッケル触媒が入った充填層反応器を用い、外部からガ

＊【請求項5】 燃料と水蒸気から水素を製造する燃料の改質方法において、燃料改質触媒層およびその下流の金属酸化物層を交互に少なくとも2組以上積層させて、燃料と水蒸気を該燃料改質触媒層に導入し、ついで生成した水素および二酸化炭素を該金属酸化物層に導入して二酸化炭素を選択的に吸収させ、該金属酸化物層から水素を流出させるとともに、該吸収の際に発生する反応熱をさらに下流の該改質触媒層に改質反応熱として供給することを特徴とする燃料の改質方法。

10 【請求項6】 燃料と水蒸気から水素を製造する燃料の改質方法において、触媒に金属酸化物を混合した燃料改質触媒層を設け、燃料と水を該改質触媒層に導入し、実質的に水素のみを該燃料改質触媒層から流出させることを特徴とする燃料の改質方法。

【請求項7】 請求項6において、反応終了後に該燃料改質触媒層を外部より加熱して、生成した金属炭酸塩の脱炭酸反応を進行させて、二酸化炭素を回収し、金属酸化物を再生させることを特徴とする燃料の改質方法。

## 【発明の詳細な説明】

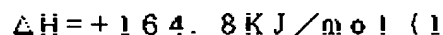
20 【0001】

【発明の属する技術分野】本発明は、燃料電池用燃料改質器に関し、さらに詳しくは金属酸化物を利用した燃料電池用の燃料改質器ならびにそれを用いた燃料改質方法に関する。

【0002】

【従来の技術】メタンやメタノール等の燃料と水（水蒸気）から水素および二酸化炭素を生成する燃料改質装置は、燃料電池に燃料ガスを供給するための装置として知られている。燃料電池は、水素を含有する燃料ガスを陰極側に供給され、酸素を含有する酸化ガスを陽極側に供給されて、両極で生じる電気化学反応により起電力が得られる。

【0003】まず、メタン含有ガスと水蒸気を用いた燃料改質装置においては、一般的に以下のメタン改質反応が行なわれ水素と二酸化炭素が製造される。



＊混合ガスが燃料電池で燃料として用いられる。

【0004】一方、メタノールと水蒸気を用いた燃料改質装置においては、一般的に以下のメタノール改質反応が行なわれ水素と二酸化炭素が製造される。

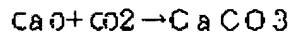
【発明が解決しようとする課題】このように上記改質反応が吸熱反応であるため、改質反応を進行させるために

【0006】そこで、本発明者は、高純度の水素が生成でき、もしくはそのうに外部加熱を必要としない燃料改質器を得るべく種々検討を行い、本発明に到達した。

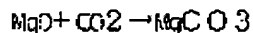
【0007】

【課題を解決するための手段】本発明における第1の態様の燃料電池用燃料改質器は、燃料と水蒸気から水素を製造する燃料改質器であって、燃料の水蒸気改質用触媒を充てんした燃料改質触媒層、燃料および水蒸気を含む改質用燃料ガスを該燃料改質触媒層に導入する改質用燃料ガス供給手段、水蒸気改質により生成する水素主成分ガスを該燃料改質触媒層から排出する改質燃料ガス排出手段、ならびに該改質燃料に含まれる二酸化炭素を吸収するために、該燃料改質触媒層の下流に設けられた金属酸化物層、を備えてなる燃料電池用燃料改質器を要旨とする。

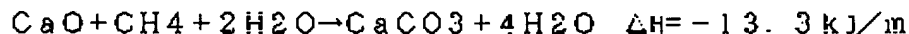
【0008】本発明において、改質される燃料は、メタン、天然ガス等のメタン含有ガス、ガソリン、ナフサ、\*



このように二酸化炭素は酸化カルシウム層に選択的に吸収され、該カルシウム層からは水素が流出する。したがって、高濃度の水素が得られるので、燃料電池の性能が向上する。さらには、二酸化炭素を大気に放出することなく回収し得る。一方、メタノールおよび水蒸気を該メタノール改質触媒層に導入すると、実用レベルの反応速度とするために好適な約200℃～300℃で水素および



このように二酸化炭素は酸化マグネシウム層に選択的に吸収され、該マグネシウム層からは水素が流出する。したがって、高濃度の水素が得られるので、燃料電池の性能が向上する。さらには、二酸化炭素を大気に放出することなく回収し得る。本発明における第2の態様の燃料電池用燃料改質器は、燃料と水蒸気から水素を製造する燃料改質器であって、燃料の水蒸気改質用触媒を充てんした燃料改質触媒層、燃料および水蒸気を含む改質用燃料ガスを該燃料改質触媒層に導入する改質用燃料ガス供給手段、水蒸気改質により生成する水素主成分ガスを該燃料改質触媒層から排出する改質燃料ガス排出手段、ならびに該改質燃料に含まれる二酸化炭素を吸収するために、該燃料改質触媒層の下流に設けられた金属酸化物層、を備え、該燃料改質触媒層および該金属酸化物層を★40

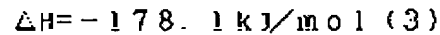


01 (5)

すなわち、13.3 kJ/molの発熱があり、この反応は外部からの熱供給なしで進行する。このように、この燃料改質器は、外部からの熱供給なしで、改質反応を白口

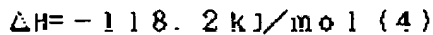
\*軽油およびLPガス、等の炭化水素類ならびにメタノールが一般的であるが、以下の説明においてはメタンおよびメタノールの場合について説明する。また、上記金属酸化物としては、二酸化炭素と反応して金属炭酸塩を生成するものが使用され、カルシウム、マグネシウム、銅、鉄およびニッケル等の酸化物が好適である。その選択は、燃料の種類等によるが、外部加熱を必要としない燃料改質器を得るために、メタンの場合には酸化カルシウム、そしてメタノールの場合には酸化マグネシウムが特に好適である。

【0009】以上のように構成された燃料改質器においては、メタンおよび水蒸気を該メタン改質触媒層に導入すると、約800℃で水素および二酸化炭素が生成される。ついでこれらを酸化カルシウム層に導入すると800℃付近で酸化カルシウムが二酸化炭素と反応して炭酸カルシウムを生成する。



※二酸化炭素が生成される(メタノール改質反応自体は反応平衡的には100℃以下でも進行する)。ついでこれらを酸化マグネシウム層に導入すると300℃～450℃付近で酸化マグネシウムが二酸化炭素と反応して炭酸マグネシウムを生成する。

【0010】



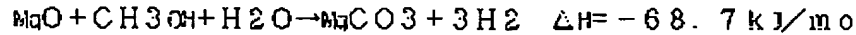
★交互に少なくとも2組以上積層させてなる、燃料電池用燃料改質器を要旨とする。以上のように構成された燃料改質器においては、メタンおよび水蒸気を該メタン改質触媒層に導入すると、約800℃で水素および二酸化炭素が生成される。該触媒層はその下流の酸化カルシウム層と交互に積層されているので、生成した二酸化炭素は下流の酸化カルシウム層で吸収される。このとき、上記のように炭酸化の発熱反応熱(178.1 kJ/mol)が生成する。この生成熱はメタン改質吸熱反応の所要熱量(-164.8 kJ/mol)より大きいので、炭酸化熱で後続の改質反応熱を供給し得る。層内全体においては、以下の反応式が成立する。

【0011】

酸化マグネシウム層で吸収される。このとき、上記のように炭酸化の発熱反応熱(118.2 kJ/mol)が生成する。メタノール改質触媒層は、炭酸



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1 (6)

すなわち、68.7 kJ/molの発熱があり、この反応は外部からの熱供給なしで進行する。このように、この燃料改質器は外部からの加熱なしに、必要な熱を自己供給しうることを実現し得る。

【0013】さらに、本発明における第3の態様の燃料電池用燃料改質器は、燃料と水蒸気から水素を製造する燃料改質器であって、燃料の水蒸気改質用触媒および金属酸化物を充てんした燃料改質触媒層、燃料および水蒸気を含む改質用燃料ガスを該燃料改質触媒層に導入する改質用燃料ガス供給手段、ならびに水蒸気改質により生成する水素主成分ガスを該燃料改質触媒層から排出する改質燃料ガス排出手段、を備えてなる燃料電池用燃料改質器を要旨とする。この態様においては、メタン改質触媒層に、触媒および酸化カルシウムが混合されて充てんされているのでより速やかな反応熱自己供給型の燃料改質が可能となる。この態様においては、メタノール改質触媒層に、触媒および酸化マグネシウムが混合されて充てんされているのでより速やかな反応熱自己供給型の燃料改質が可能となる。

【0014】

【発明の実施の形態】以下、まず本発明において燃料ガスとしてメタン含有ガスを用いる場合について図面とともに説明する。図1は、本発明における上記第1～3の3つの態様の改質器を示す模式図である。aは加熱を要する二酸化炭素吸収型の改質器であり、メタン含有ガスとしてメタンが水蒸気とともに反応管(1)に導入される。反応管(1)は加熱炉(4)で所定温度に保持されており、触媒層(2)には水蒸気改質用触媒としてNi担持アルミナが充てんされている。この触媒層において約800℃で改質反応されて、水素および二酸化炭素を含む生成ガスが流出し、下流の酸化カルシウムを充填された金属酸化物層(3)に導入される。そこでは二酸化炭素が選択的に吸収され、金属酸化物層からは高濃度の水素が流出する。上記触媒は、上記の、Niに限定されるものではなく、さらに担体もアルミナに代えてシリカ等を使用しうる。bはNi担持触媒層(2)と酸化カルシウム充填された金属酸化物層(3)を交互に2組以上積層した積層型改質器を示し、cはNi担持アルミナと酸化カルシウムを混合した触媒/金属酸化物混合層(5)を有する混合型改質器を示す。d、cは、いずれも反応熱自己供給型であり、基本的に加熱を必要とせず、スタート時のための予熱器(図示せず)を備えるにすぎない。

【0015】本発明の燃料改質器において、反応管の燃料改

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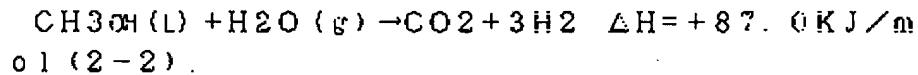
取されその濃度が減少するために、平衡論的に一酸化炭素の二酸化炭素化の反応がより良く進行する。このために一酸化炭素の発生が抑制される。一酸化炭素は燃料電池の電極触媒(白金系)を被毒し電池特性を低下させるので通常、改質器の下流に一酸化炭素変成器が設けられているが、本発明によればこの変成器への負荷を減少ないしはそれを不要にしうる。

【0016】図2は、本発明の燃料改質器における主要反応の進行性を化学反応平衡線により示すものであり、酸化カルシウム/二酸化炭素、酸化カルシウム/水および燃料改質反応の平衡関係を示す。酸化カルシウム/二酸化炭素系は当該の反応であり、酸化カルシウム/水系は使用するガスから予想される競合反応である。縦軸の圧力Pは、各反応における二酸化炭素圧力、水蒸気圧力を示し、分解度(左方向反応)の進行度合いを示す(Pが大きいほど良く分解する)。改質反応のみは反応平衡定数Kを示す。たとえば、700℃付近では炭酸カルシウムはほとんど分解しない。すなわち酸化カルシウムの炭酸化が良く進む。また、燃料改質反応は右方向(水素生成側)に進行することがわかる。一方、水酸化カルシウムはほとんど分解して酸化カルシウムとなるため、酸化カルシウムへの水の吸収はほとんど起こらない。このことからこの温度域では改質反応が良く進み、生成した二酸化炭素は酸化カルシウムと炭酸化反応を行なうことが熱力学的に確認できる。

【0017】さらに図3は、反応初期温度650℃において、炭酸化圧力の変動に伴う反応層温度変化を示す。すなわち、酸化カルシウム反応試料約1kgの充てん層型反応器において、初期650℃の反応層に反応時間0分に二酸化炭素を導入すると速やかに反応が進行する。そして、反応熱により反応層は急激に900～1000℃に温度上昇する。このことから、約700～800℃付近での二酸化炭素の酸化カルシウムへの吸収(炭酸化)は十分に進行し、自己反応熱供給が可能であることが示される。

【0018】一方、本発明においてメタノール燃料を用いる場合には、上述のとおりメタン/酸化カルシウムにかえてメタノール/酸化マグネシウムにかわり反応温度が異なるが、上記図1a、bおよびcはそのまま該当する。図4は、メタノール燃料を用いる場合において、本発明の燃料改質器における主要反応の進行性を化学反応平衡線により示すものであり、酸化マグネシウム/二酸化炭素、酸化マグネシウム/水および燃料改質反応の可

分解する)。改質反応のみは反応平衡定数 $K$ を示す。たとえば、300℃付近では炭酸マグネシウムはほとんど分解しない。すなわち酸化マグネシウムの炭酸化が良く進む。また、燃料改質反応は右方向(水素生成側)に進行することがわかる。一方、水酸化マグネシウムはほとんど分解して酸化マグネシウムとなるため、酸化マグネシウムへの水の吸収はほとんど起こらない。このことからこの温度域では改質反応が良く進み、生成した二酸化炭素\*



メタノール、水がともに液相の場合、 $\text{CH}_3\text{OH}(\text{L}) + \text{H}_2\text{O}(\text{L}) \rightarrow \text{CO}_2 + 3\text{H}_2 \quad \Delta H = +131.0 \text{ KJ/mol} \quad (2-3)$ である。式(6)であらわされる $\text{Mg}$ の炭酸化での発熱量は、式(2)の反応に必要な熱量よりも大きく、発熱温度も約300℃である。したがって、式(2)の改質反応熱は十分に供給可能であり、外部加熱を必要としない自力反応も可能である。さらに、式(6)の発熱量は式(2-2)の反応に必要な熱量よりも大きい。そのため、その余剰熱は、メタノールの気化に利用できる。一方、水の気化熱も含む式(2-3)の反応には、式

(6)の熱量は不十分であるが、燃料電池(たとえば自動車用燃料電池)からの廃熱を併用することで式(2-3)の自力進行も可能となる。

【0020】上記のとおり、本発明によれば高純度の水素が生成でき、もしくはそのうえに外部加熱を必要としない燃料改質器を提供しうる。

\*は酸化マグネシウムと炭酸化反応を行なうことが熱力学的に確認できる。

【0019】式(6)で生成した炭酸マグネシウムは加熱により高圧で分解して酸化マグネシウムに戻るため、再度の燃料改質に用いることができる。なお、式(2)であらわされる反応熱は、反応原料の相により異なる。たとえば、メタノールが液相の場合、

※【図面の簡単な説明】

【図1】本発明の燃料改質器の実施態様を模式的に示す図である。

【図2】本発明の燃料改質器における主要反応の化学反応平衡線を示す図である。

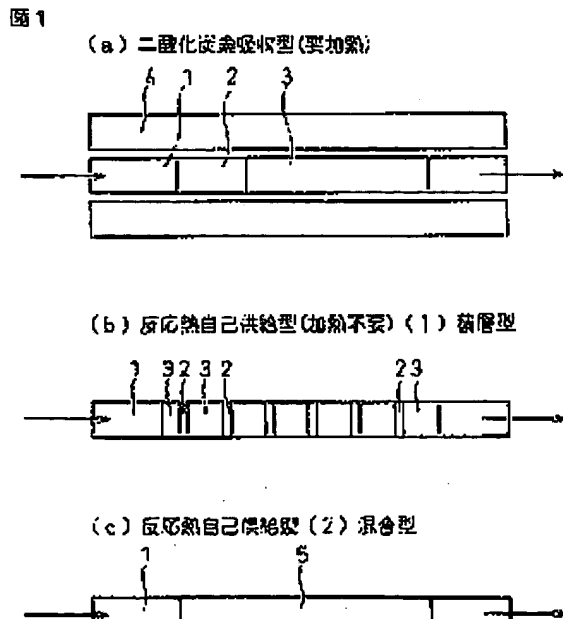
【図3】本発明の燃料改質器において、炭酸化圧力の変動に伴う反応層温度の変化を示す図である。

【図4】本発明の燃料改質器における主要反応の化学反応平衡線を示す図である。

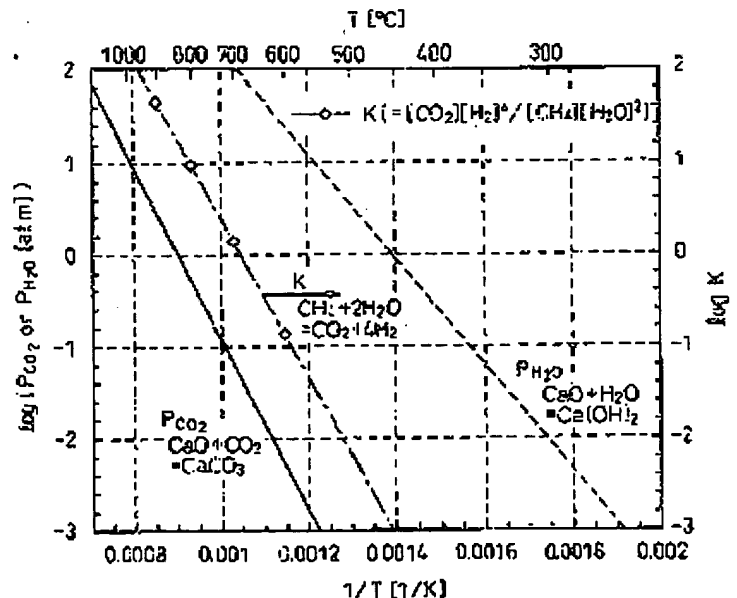
【符号の説明】

- 1…反応管
- 2…触媒層
- 3…金属酸化物層
- 4…加熱炉
- 5…触媒/金属酸化物混合層

【図1】

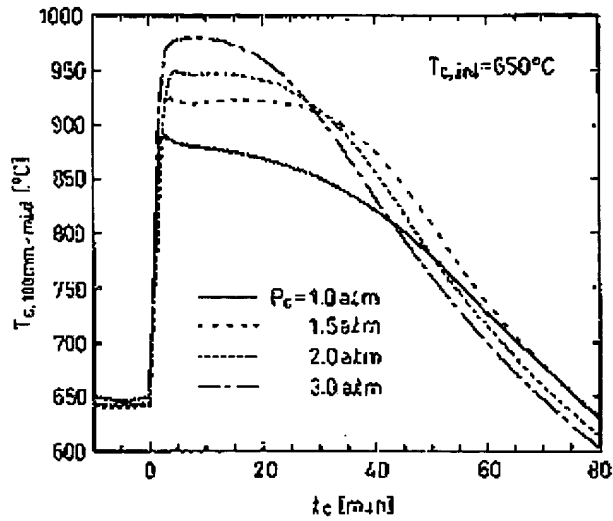


【図2】



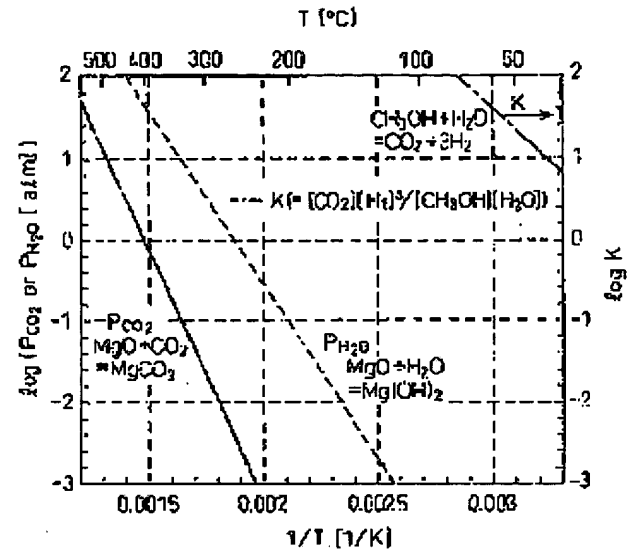
【図3】

図3



【図4】

図4



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